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カレリア地方産出鉍石シュンガイト中のフラーレン成因調査

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カレリア地方産出鉍石シュンガイト中の フラーレン成因調査

(研究課題番号：14404013)

平成14年度～16年度科学研究費補助金
(基盤研究(B)(1)) 研究成果報告書



平成17年5月

研究代表者 田中一義
(京都大学工学研究科教授)

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(1) 国際シンポジウム “Shungite Symposium in Kyoto 2004” 開催（京都, 2004）

(2) ロシアの大地に C₆₀ を追って, 田中一義, 化学, **58**, 17 (2003).

(3) Occurrence and Lithofacies of Shungite: Early Proterozoic Carbon-Rich Rocks from Karelia, Northwestern Russia, K. Yoshida, K. Chijiwa, K. Hoyanagi, K. Tanaka, T. Yoko, K. Yanagisawa, A. Ito, and E. Osawa, *Journal of the Geological Society of Japan*, **110**, I (2004)

(4) Existence of C₆₀ in Shungite-Type I Rocks, S. Ohmori, T. Hirayama, A. Ito, and K. Tanaka, *Abst. 26th Fullerene-Nanotubes General Symposium*, **26**, 69 (2004)

(5) 北西ロシア、カレリア産シュンガイトの産状と化学組成, 吉田孝紀, 保柳康一, 福島和夫, 千々和一豊, 田中一義, 地球惑星科学関連学会 2004 年合同大会予稿集, G16 (2004).

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序 言

本研究は平成 14-16 年度科学研究費補助金基盤研究(B)(1)に基づく海外調査研究として実施したものである。地域としてはロシア連邦カレリア共和国のオネガ湖北西部付近の下部原生界 Karelian Super Group 中のシュンガイト鉱石産出地 Shunga ほかにおいて採取した鉱石試料の分析を行い、特にナノ分子の代表格であるフラーレン分子 C_{60} 含有の確認とその成因調査を精力的に行った。

一般にこの鉱石群は黒色、細粒かつ緻密な岩石で、最大 98wt% もの炭質物を含む。本研究においては、約 20 億年前（先カンブリア時代）に堆積した炭素富裕鉱物層中でフラーレン分子が存在していることを確認できた Type I シュンガイト (75-98wt%C) に加えて、上記オネガ湖北岸地域および西北地域 Shunga, Zazhogino, Maksovo で産出される、Ludicovian Group での低炭素含有鉱石（タイプ II-V; 10-75wt%C）の産状と周辺の岩石層の研究の総括も行った。Karelian Super Group は層序的下位より、Jatulian, Ludicovian, Kalevian, Vepsian の各グループに区分されている。Ludicovian Group の玄武岩の Sm-Nd 年代は 1.98Ga である。

本研究で得られた主要な結論として、低炭素含有シュンガイトは初生的に有機物に富む硅質な堆積岩を起原とすると考えられ、Type III シュンガイト (20-35wt%C) などの中程度の炭素含有量を示すものは、初生的に炭素質な堆積岩と火山岩類の反応によって富化された結果による可能性がある。Type I-II (35-98wt%C) シュンガイトは何らかの状況で濃集した炭質物が流体として再移動した結果の産物と考えることができる。しかしながら、堆積物中に本来存在した炭質物の起原や、火山岩類を伴わない大量の Type III-IV (10-35wt%C) シュンガイトの起原は現時点では不明であり、なお調査を要すると考えている。

なお本科学研究費によるものとして、平成 16 年 12 月 3 日に京都大学において、海外共同研究者のナタリア N. ロシュコワ博士を招いて西側諸国としては初のシュンガイトシンポジウムを開催し、化学的・鉱物的・地質学的な各視点からの活発な討論を行ったことも特筆に値する。短い期間であったが、海外現地調査を含めて有意義な研究を我が国で初めて展開でき、ロシア科学アカデミーと我が国研究者間の良好な共同研究体制を築くことも可能となるなど、実りの多い研究を遂行できた。

研究代表者 田中一義

Shungite Symposium in Kyoto 2004

December 3, 2004

Kyoto University, Katsura Campus

Room #A2-307

Shungite Symposium in Kyoto, 2004

Kyoto University, Katsura Campus, Room #A2-307

13:00-17:10

- 13:00 Opening (K. Tanaka) +
Amount of C₆₀ in Shungite Rocks (K. Tanaka, S. Ohmori, T. Hirayama, and A. Ito)

(Chairperson: E. Osawa)

- 13:30 Study of Aqueous Dispersions of Shungite Carbon Nanoparticles: Results and Perspectives (N. N. Rozhkova)

- 14:10 Stable Carbon Isotope Ratio ($\delta^{13}\text{C}$) of the Shungite and Its Implication for the Carbon Origin (K. Hoyanagi, K. Yoshida, and K. Fukushima)

- 14:30 The Variation in REEs (Rare Earth Elements) Patterns of the Karelian Shungite, Northwest Russia (K. Yoshida)

- 14:50 Mineralogical Study on the Shungite Rocks (T. Yoko)

+++++

- 15:10-16:00 Break + Walking in the Katsura Campus

+++++

(Chairperson: N. N. Rozhkova)

- 16:00 Organopetrography of Shungite from the Karelia Republic, Russia (K. Chijiwa)

- 16:20 Structural Similarity between Shungite and Soot (E. Osawa)

- 16:40 Hydrothermal Treatment of Shungite Rocks (K. Yanagisawa and T. Fujino)

- 17:00 Closing Remarks (E. Osawa)

#Please leave ca. 5 minutes for discussion within your presentation time.

#We will use the Shuttle Bus from the Katsura to the Main Campus of Kyoto University starting at 18:20 after the Symposium.

These researches are based on the agreement between Department of Molecular Engineering, Kyoto University, Japan and the Institute of Geology, Karelian Research Center, Russian Academy of Sciences.

This Symposium is sponsored by Grants-in-Aid for Scientific Research (B)(1) (No. 14404013) from MEXT (Ministry of Education, Culture, Sports, Science and Technology) and JSPS, and partly by 21st century COE, Chemistry Network, Kyoto University.

Amount of C₆₀ in Shungite Rocks

Kazuyoshi Tanaka, Shigekazu Ohmori, Takamasa Hirayama, and Akihiro Ito

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Shungite is the black Precambrian rock contains abundant carbon component and is produced in the Karelia region in northwestern Russia near the border of Finland. There are several types of Shungite rock depending on the amount of carbon included. It is of interest that Shungite-type 1 (amount of carbon component up to 92-98 %) produced in the Shunga deposit near the north shore of the Lake Onega in Karelia could contain natural fullerene (C₆₀), which was reported in 1992 by means of High Resolution Transmission Electron Microscopy (HRTEM) as well as Fourier Transform Mass Spectroscopy (FTMS) [1]. On the other hand, however, it has been claimed that these measurements can damage the original carbon ingredient to generate fullerene skeleton in the apparatus chamber itself [2]. In our present research we undertake the verification of existence of fullerene in Shungite-type 1 with milder and acceptable measurement.

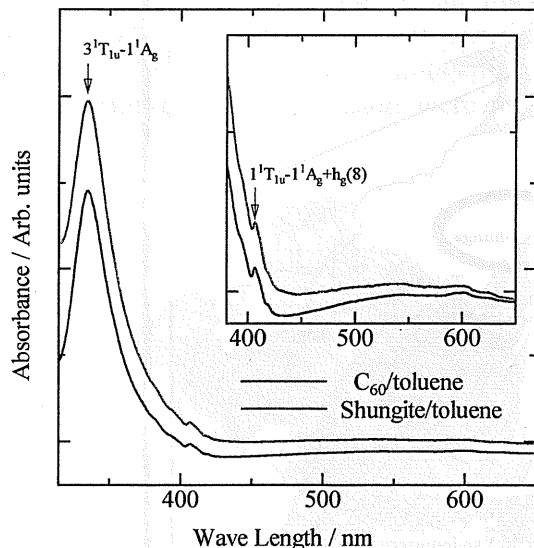


Fig. 1. UV-vis spectra of Shungite-type 1 sample from the Shunga deposit and pure C₆₀.

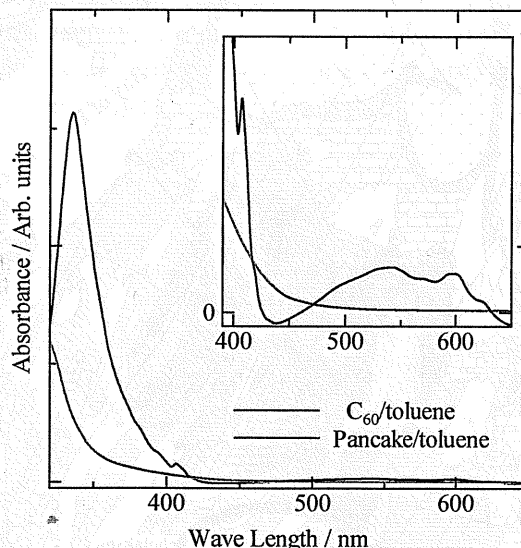


Fig. 2. UV-vis spectra of Shungite-type 1 (Pancake-form) sample from the Kondpoga deposit and pure C₆₀.

We check the collected Shungite-type 1 sample, cracked and washed in 10 % HCl_{aq} and then ground with pestle and mortar less than 100 μm in diameter, with the

UV-vis absorption spectroscopy as well as ^{13}C -NMR and Atomic Force Microscopy (AFM). Figure 1 shows the UV-vis spectrum of Shungite-type 1 sample as the toluene-extracted solution (red curve) with the standard C_{60} sample solution (black curve). It is obvious that Shungite-type 1 sample contains C_{60} as well and the estimated amount of C_{60} by integration of the signal has given the weight ratio of 19 ppm. On the other hand, the ^{13}C -NMR and AFM failed to find existence of C_{60} obviously probably because of less content of the limitation. Moreover, we have not succeeded in finding out C_{60} , which suggest its absence in the Pancake-form Shungite-type 1 rock in the Kondpoga deposit as shown in Fig. 2.

Reference

1. P. R. Buseck et al., *Science*, 257, 215(1992).
2. P. J. F. Harris, "*Carbon Nanotubes and Related Structures*," Cambridge University Press (1999), p.34.

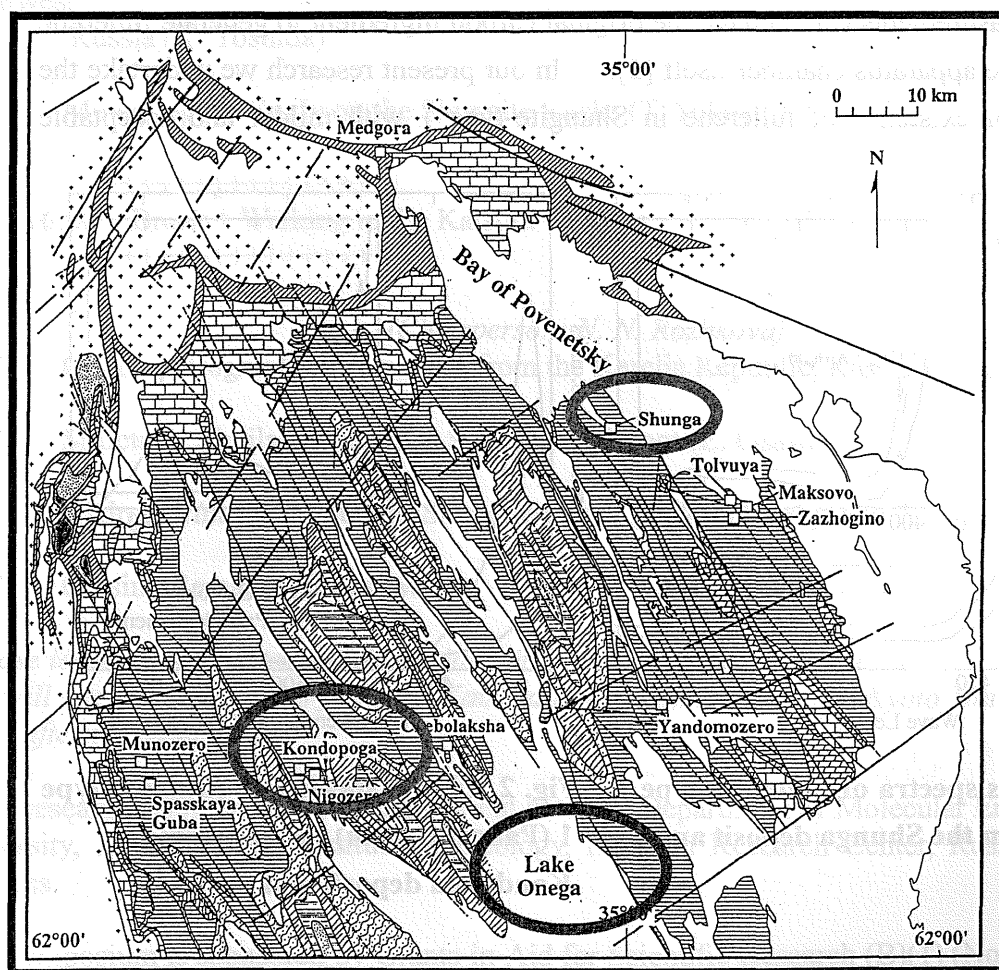


Fig. 3. Northeast-shore area of Lake Onega.

Study of Aqueous Dispersions of Shungite Carbon Nanoparticles: Results and Perspectives.

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Shungite carbon impregnating different rocks of the lake Onega region has been a target of scientific interest for more than two centuries. Nongraphitic shungite carbon (SC) from different deposits of the region is characterized by similar globular structure at the nano-scale level. It displays inert properties but can be modified under steam conditions. SC properties depend to a large extent on the particular method of its treatment. Applying steam treatment to SC from the Shunga deposit, physical chemical properties of more active species of SC from Maksovo and Nigozero can be obtained in the former [1].

Structural parameters of bulk SC are stable up to 727 K in vacuum, whereas globular units of SC are metastable. Merging of the globules takes place at lower temperatures than similar association of carbon black particles. Dry grinding of SC leads to transformation of the globules into clusters composed of polyhedral particles and resembling the known "grapes" of carbon blacks. Similar entities were found in lydite (shungite rock with carbon content <5 wt.%). An autoclave treatment helps to release such particles in the cluster form. Their properties were similar to the active carbon black of the acetylene type [2].

It was intriguing that SC originated from algae in mild aqueous conditions, according to geological data, had structural characteristic features similar to those of carbon black. Factors affecting formation and transformation of carbon black aggregates may influence SC structural organization, too. Water would play a significant role in it.

Water and some other polar solvents were used to disperse SC for TEM and surface preparation of SC in AFM study. An average particle size of globular units (~26 nm) of SC and the size distribution of their clusters were determined (Fig1a).

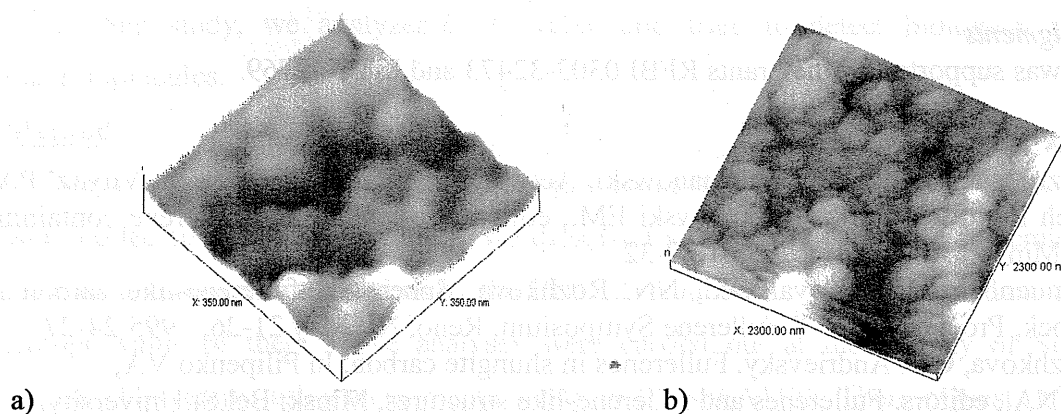


Fig.1. a) AFM image of SC fracture (Shunga), b) AFM image of precipitated aqueous dispersion of SC

The structure and dynamics of formation of a nanoscale carbon net can be described through a comparison with fullerene-like particles and C_{60} , because they are morphologically and genetically similar. SC units have multi-layered structures composed of graphite-like planes, with structural and morphological features of aggregated giant fullerenes or multi-layered fullerenes. Aqueous molecular colloidal solution of fullerenes was used as the

standard in studying components of SC aqueous dispersion prepared by the same method as the fullerene solution. It was the only way of reproducible fullerene extraction from SC [3].

The aqueous dispersion of SC mostly consists of carbon nanoparticles which predetermine reactivity of the dispersion and SC itself [4].

Recent results on the study of SC aqueous dispersion are the subject of the present paper.

The aqueous dispersions were prepared by ultrasonic treatment of SC (Shunga deposit) powder in water with addition of toluene/propanol at 22 kHz and were stable for several months.

Spectral methods (UV, FTIR, and EPR) were used to characterize the SC dispersion. TEM, and AFM were applied to determine the morphology and dimensions of clusters and nanoparticles in concentrated gel or in films prepared from the aqueous dispersions.

An average radius of carbon clusters determined by DLS was 35 ± 5 and 95 ± 5 nm for fullerene and SC dispersions respectively. Polydispersity was the same in both cases.

The phase precipitated from aqueous colloids of fullerenes at ambient conditions was composed of mainly globular particles 20-70 nm in size. Precipitated SC dispersion contains nanoparticles, amorphous carbon and fullerene-containing phase. The size distribution of nanoparticles depends on the drying conditions.

The next morphological level was measured by AFM. Particles were less than 330 nm with an average dimension of 60-80 nm (Fig.1b).

The FTIR spectrum of SC gel is characterized by very rich structure in comparison with SC powder in a higher frequency range ($1220-500 \text{ cm}^{-1}$).

The aqueous dispersion of SC is a very challenging object. Biological aspects of fullerenes and carbon nanoparticles can be studied only in the form of aqueous solutions. Their detailed study will give answer to some open issues:

- How to preserve reactive fullerenes and nanoparticles,
- What is the origin and formation mechanism of SC nanoparticles.
- Is reconstruction of SC formation a way to a new technology?

Acknowledgments

The work was supported by the grants RFBI 0303-32473 and ISTC #2769.

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Stable Carbon Isotope Ratio ($\delta^{13}\text{C}$) of the Shungite and Its Implication for the Carbon Origin

Koichi Hoyanagi, Kohki Yoshida, and Kazuo Fukushima

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Introduction

Shungite rocks are general term for the carbon rich rocks of the lower Proterozoic Karelian Super Group in Karelia (eastern Fennoscandian Shield). Carbon contents of the Shungite rocks are generally several % to 90 % or over. The shungite rocks are classified into five categories (Type 1 to 5) by carbon content. Type 1 has the highest carbon content and it is more than 75 % in weight. The shungite rocks are considered to be formed in 2 billion years ago, based on the study of radiometric isotope age.

The formation process of the shungite rocks has been well studied by the scientists in the Karelian Science Center, Russian Academy of Science. According to their precise geological, geophysical and geochemical studies, they have been considered to be originated from coalification of organic hydrocarbon in oil reservoir. Stable carbon isotope ratio ($\delta^{13}\text{C}$) show -25 to -40 ‰ (Buseck et al., 1997).

In this study, we analyzed $\delta^{13}\text{C}$ value and tried to detect biological marker macromolecules.

Method

We analyzed 10 samples of the Shungite rocks and related siliceous shale, which were collected in 2002 and 2003. We dissolved silicate and carbonate minerals from the rock and concentrated carbon by the HF/HCl treatment. We analyzed stable carbon isotope value of them. The analyses were carried out at the Faculty of Science, Shinshu University, using an elemental analyzer (FlashEA1122, ThermoQuest Ltd.) and a mass spectrometer (Delta Plus, ThermoQuest Ltd.). A few milligrams of each sample was heated to 950°C in the furnace of the element analyzer, and the resulting purified CO_2 gas was fed directly into a mass spectrometer using a pure helium carrier gas. Carbon isotope results are expressed as per mil (‰) relative to the V-PDB standard. We measured a working standard (Atropine; $\delta^{13}\text{C} = -23.2\text{‰}$) with every eight samples. The analytical precision was 0.1‰ in carbon for C.

Pyrolytic GC/MS analyses were carried with a GC/MS analyzer (HP6890GC-5873MSD) at the Faculty of Science, Shinshu University to detect biological marker macromolecules.

Results and discussion

Three samples of the Type 3 shungite rocks show -25 to -27 ‰ of the $\delta^{13}\text{C}$ values, three samples of the Type 1 show -37 to -38 ‰, and three samples of the Type 3 show -40 to -42 ‰ (Fig. 1). The $\delta^{13}\text{C}$ values of -25 to -27 ‰ coincide with these of the higher land plants, but they did not appear in 2 billion years ago. Organic carbon produced by cyanobacteria is considered to show -15 to -35 ‰ of the $\delta^{13}\text{C}$ values. We also concluded that the carbon of the shungite rocks is originated from organic carbon. The negative values such as -40 to -42 ‰ might be caused by the activity of methane bacteria in anoxic conditions.

We detected very small quantity of n-alkanes by the pyrolytic GC/MS analyses. We cannot deny a contamination during the analytical processes with these small values. Biological marker macromolecules might be decomposed by high temperature during diagenetic and metamorphic processes.

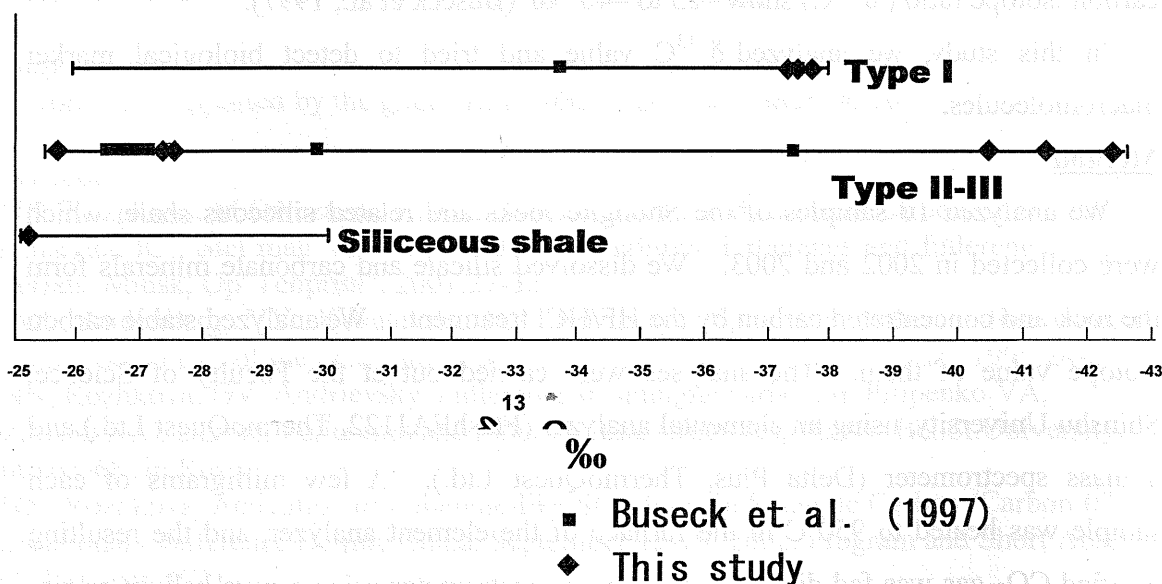


Fig. 1. $\delta^{13}\text{C}$ values of the shungite rocks in Karelia.

The Variation in REEs (Rare Earth Elements) Patterns of the Karelian Shungite, Northwest Russia

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Japan

Shungite are carbon-rich rocks found in the Lower Proterozoic Karelian Super Group that is widely distributed in the area surrounding the northwest region of Lake Onega in the Karelian Republic of northwestern Russia. These are black, fine-grained rocks that are traditionally divided into five types on the basis of the carbon content, i.e., type I (carbon content 98 — 75 wt%), II (75 — 35 wt%), III (35 — 20 wt%), IV (20 — 10 wt%) and V (less than 10 wt%), regardless of the original lithology. The types I and II occur as a dyke or as sheet-like bodies in the specified area, while the other types are more widely distributed and are confirmed to be host rocks of types I and II.

Rare earth elements (REEs) of the type I, II, III, and V shungites (type IV is not examined), collected from the Shunga, Maksovo and Zazhogino areas, were the subjects of this study. Prior to the analysis, the chemistry of the major and trace elements, organic carbon content, and loss on ignition (LOI), which is related to organic and carbonate contents is measured. The REE patterns, where the abundances were normalized to those of the chondrite (CH) and Post-Archaean Australian shale (PAAS) and plotted on a logarithmic scale against the atomic number, show variations. From the above-mentioned, the following matters have been clarified. (1) In CH-normalized diagram abundant Cerium depletion of (negative Ce anomaly) was observed in each REE pattern of type I and II shungites. (2) In the diagram, more conspicuous depletion of europium (negative Eu anomaly) was observed in most of type I, II, and III shungites, the exception being a type III sample originating from glassy basalt. (3) The siliceous shale, which is considered to be correlated to type V has a flat pattern with slight negative Ce and positive Eu anomalies. The overall variation in the REE patterns of both type II and III shungites is similar to that in type I excluding the presence of Ce anomalies in CH-normalized diagram. (4) In PAAS-normalized diagram distinct enrichment of ytterbium (positive Yb-anomaly) was also found in most of samples.

Previous studies on the controversial issue of REE mobility during metamorphism show that the behavior of the REEs during early diagenesis and metamorphism is very complex. However, various REE abundances in the type III shungites, despite original lithologies, confirm that the REEs cannot be mobilized sufficiently to achieve a uniform

REE distribution.

It is known that Ce tends to oxidize from the trivalent state as an unstable dissolved material to the tetravalent state as solid $\text{Ce}(\text{OH})_4$ under oxic conditions. This implies that oxic seawater is more depleted of Ce content. Under anoxic conditions, sediments have a negative Ce anomaly due to the release of the trivalent state of Ce into seawater. A type I negative Ce anomaly, showing the depletion of Ce under an anoxic condition indicates that the redox potential of the environment was sufficiently high to reduce trivalent states to tetravalent states of Ce. On the other hand, the redox potential of type III shungite was perhaps not sufficiently high, and these samples were associated with conditions considered more oxic.

Meanwhile, Eu anomaly in sedimentary rocks could possibly be the result of enrichment of plagioclase contents, sedimentation in alkaline pore water of anoxic marine conditions, or the interaction of the rocks with fluids. A slight positive Eu anomaly in type V suggests that changes in the REE contents of the sediments could not be attributed to the diagenetic processes. The coexistence of the slight anomaly of gassy basalt and the distinct anomaly of most of the shungites might be related to the composition of original lithology and not to the magmatic and/or fluidal interaction.

Although it is considered that Yb is apt to be reduced to the divalent state from the trivalent state under the reducing conditions, exact reason of the positive Yb anomaly is not clear.

A variety in the REE patterns of shungites suggests that type I was formed under different geochemical conditions as compared to other types of shungites, although the original carbonaceous material has common geochemical characteristics in REE pattern. Further, the depositional condition of type III was not clarified by REE pattern, however, the enrichment of Yb might be important as a key for the settlement.

Mineralogical Study on the Shungite Rocks

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Shungite rocks (called shungite carbon; ShC) are two billion years old pre-cambrian carbon-containing rocks, which are produced in Karelia, Russia (1, 2). In recent years, these rocks have attracted attention, because the origin of such organic matters in the meta-anthracitic stage of coalification is still not well-known (1, 2), and moreover the presence of C₆₀ and C₇₀ fullerenes in them has been experimentally confirmed (3, 4). It is, therefore, of great importance to know where the carbonaceous materials came from and what happened to them during the formation process. Shungite rocks are classified into three types based on the form of manifestation: 1) *a protosedimentary type*, 2) *a migratory type*, and 3) *a mixed type* of 1) and 2). Moreover, these three types of shungite rocks are subdivided on the basis of the content of organic carbon (C_{org}) into five types: Shungite-I (natural bitumen, anthraxolite, C_{org} > 95%) and Shungite II-V (sedimentary, volcano-sedimentary and chemically precipitated rocks that make up 35-70%, 20-35%, 10-20% and < 10%, respectively). In the present study, crystalline phases precipitated in the different shungite rocks and their contents were systematically examined in terms of an X-ray diffraction analysis and an X-ray fluorescence analysis in order to know the role of each substance.

Table 1. Major crystalline phases precipitated and chemical composition of respective elements in various shungite rocks

	C	Mg	Al	Si	P	S	Cl	K	Ca	V	Fe	Ni	Cu	Zn		C _{org}	Phases
ShungiteType1	96.5			0.2	0.0	0.9	1.3	0.1	0.0	0.4	0.2	0.3		0.1	(wt%)	?	a-C >> C(graphite)
Cave	98.9			0.1	0.0	0.3	0.4	0.0	0.0	0.1	0.0	0.1		0.0	(mol%)		
ShungiteType1	76.8	0.5	0.6	0.7	0.1	1.2		0.3	16.2		0.9	1.3	0.5	0.9	(wt%)	?	a-C
Road-side	91.7	0.3	0.3	0.4	0.0	0.5		0.1	5.8		0.2	0.3	0.1	0.2	(mol%)		
	4.6	17.4	6.6	33.3	0.1	8.9		15.3		1.6	11.6	0.2		0.1	(wt%)		SiO ₂ (quartz) >> a-C >
ShungiteType2	11.2	20.7	7.1	34.3	0.1	8.1		11.4		0.9	6.0	0.1		0.1	(mol%)	?	C(graphite), FeS ₂ , unknown phases
	71.2	0.9	7.4	10.2		3.6	0.3	3.9			2.5				(wt%)	?	C(graphite) >> SiO ₂ (quartz) > FeS ₂
Maksova	86.4	0.5	4.0	5.3		1.6	0.1	1.4			0.7				(mol%)		a-C, unknown phases
	6.3	0.2	0.7	91.7	0.2	0.2		0.3			0.4				(wt%)	×	SiO ₂ (quartz) >>
Tsutsugino	13.6	0.2	0.7	84.8	0.2	0.2		0.2			0.2				(mol%)		C(graphite)
	7.6	7.9	20.2	45.4	1.2	1.4		5.6	0.4		10.0	0.2	0.2		(wt%)	?	SiO ₂ (quartz) >> a-C >
Zazhogino	16.9	8.7	20.0	43.2	1.1	1.2		3.8	0.3		4.8	0.1	0.1		(mol%)		C(graphite)

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Organopetrography of Shungite from the Karelia Republic, Russia

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The Karelian shungite rocks are prominent in the Lake Onega region, and intercalated within the greenschist-facies Lower Proterozoic - Ludicovien rocks (2.0 to 2.1 Ga). They are grouped into five types (I, II, III, IV, and V) on the basis of their carbon contents. The first report of the occurrence of natural fullerenes was reported from type-I shungite rocks containing carbon 75 to 98 wt% (Buseck et al, 1992).

From the field observation is confirmed the following three modes of occurrence of type-I shungite ; 1) thin layer (type Shunga deposit), 2) gravel (Kondopoga deposit), 3) laminae/lens/fragments (Zazhogino deposit). The feature of occurrence and sedimentary sequence suggests that the type-I shungite originated from the sedimentation of organic matter.

The optical and chemical analyses of selected type-I shungite samples have been performed.

Type-I shungite shows evenly structureless surface under the microscope, and is quite close to anthracite or meta-anthracite in appearance. Judging from the result of reflectance measurement, type-I shungite show an uniaxial nature in spite of high rank, and that an optical axis is perpendicular to the bedding plane. The appearance of optical anisotropy is in medium level. This may mean that the type-I shungite has been scarcely subjected to tectonic stress.

The carbon content of selected type-I shungite samples ranges from 91.46 to 93.39%. The reflectance values of type-I shungite are actually higher than ones expected from the carbon contents in coal series. The relationships between the carbon content and H/C atomic ratio of type-I shungite are plotted outside of the general trend of coal series. The characteristic of lower H/C atomic ratio of type-I shungite results in the deterioration of calorific value in comparison with coal series.

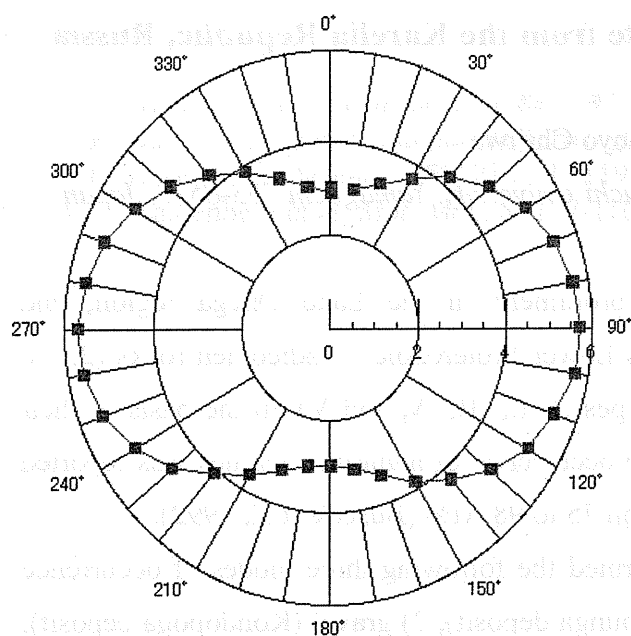


Fig. 1. In polar coordinate is represented reflectance on polished surface almost perpendicular to the bedding plane of shungite through the rotation of stage.

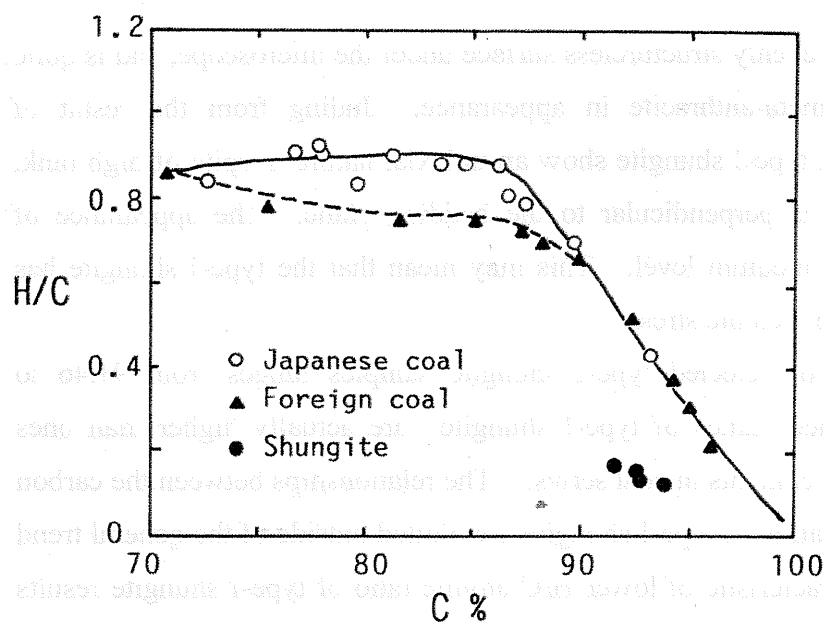


Fig. 2. Relationship between H/C atomic ratio and carbon content of shungite and coals. Note the lower value of H/C of shungite in comparison with coals.

Table 1 Results of chemical analyses of selected shungite type I samples

sample			Type Shungite type I (layer) from adit of Shunga Deposit				"Pancake-like" shungite type I (gravel) from dump at Kondopoga				Method of Analysis
			A		B		C		D		
analytical base			(a.d)	(d.a.f)	(a.d)	(d.a.f)	(a.d)	(d.a.f)	(a.d)	(d.a.f)	
Proximate analysis	Moisture	%	2.5	—	2.9	—	6.3	—	3.4	—	JIS M 8812
	Ash	%	2.1	—	1.9	—	4.0	—	20.6	—	
	Volatile matter	%	9.2	9.6	9.5	10.0	9.1	10.1	9.6	12.6	
	Fixed carbon	%	86.2	90.4	85.7	90.0	80.6	89.9	66.4	87.4	
	Fuel ratio		9.4	9.4	9.0	9.0	8.9	8.9	6.9	6.9	
	Calorific value	cal/g	7,160	7,510	7,110	7,470	6,650	7,410	5,450	7,170	JIS M 8814
		J/g	29,970	31,440	29,760	31,270	27,840	31,020	22,810	30,010	
Ultimate analysis	Ash	%	2.2	—	2.0	—	4.3	—	21.3	—	JIS M 8813
	C	%	91.34	93.39	90.84	92.69	88.51	92.49	71.98	91.46	
	H	%	0.97	0.99	0.99	1.01	1.18	1.23	1.15	1.46	
	O	%	4.43	4.54	5.31	5.43	5.70	5.96	5.36	6.81	
	N	%	0.67	0.68	0.65	0.66	0.21	0.22	0.15	0.19	
	Total Sulfur	%	0.45	—	0.39	—	0.10	(0.10)	0.06	(0.08)	
	combustive S.	%	0.39	0.40	0.21	0.21	tr.	tr.	tr.	tr.	
	non-comb. S.	%	0.06	—	0.18	—	tr.	—	tr.	—	
	(sulfur in ash)	%	(2.59)	—	(9.15)	—	—	—	—	—	

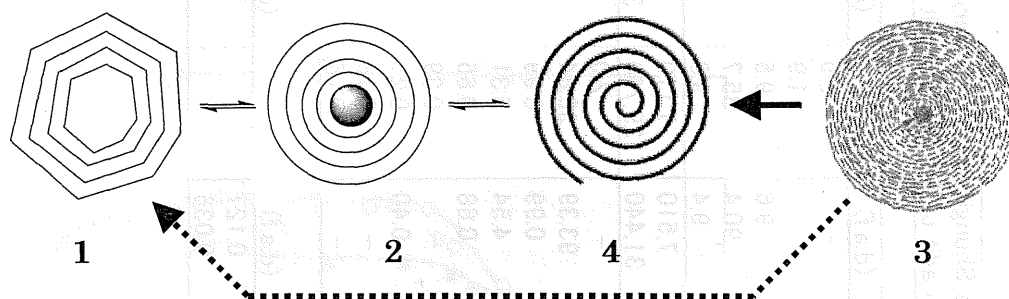
	(d.a.f)	(d.a.f)	(d.a.f)	(d.a.f : dry ash free)
H/C atomic ratio	0.127	0.131	0.160	0.192
O/C atomic ratio	0.036	0.044	0.048	0.056

Structural Similarity between Shungite and Soot

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Primary particles of shungite and soot have common and distinct structural features related to multi-shell fullerene or carbon nano-onion. In the case of shungite, the primary particles are polyhedral onions with void **1** [1], a morphology known to form when spherical multi-shell fullerenes (**2**, Ugarte's ultimate fullerene) have been exposed to very high temperatures. On the other hand, the primary particles of carbon blacks **3** (pure soot), are highly defective Ugarte fullerenes and/or its spiral valence isomer or spiroid **4** [2]. We found that their structural defects can be removed by irradiation of high-current/high-voltage electron beam to give almost flawless **2** through and that this transformation passes through **4** as the intermediate. The discovery of **4** solved long-standing riddles on the growth and formation of soot [2].



Mechanistic details of the transformation from **2** to **1** is still unclear but it is likely that large-amplitude thermal vibration of **2** at high temperatures will induce Pacman opening of outer shells [3] or extensive loosening of spirals during the structural annealing. As the consequence some of the inner contents of amorphous carbon atoms will escape to outside to cause deficiency of carbon atoms as the crystallization proceeds from outer to inner shells.

A logical extension of the close structural and mechanistic connection between shungite and soot will be to hypothesize that shungite originated from soot, the product of incomplete combustion or pyrolysis of carbonaceous materials. Soot is a likely origin of any sp^2 -hybridized form of carbon occurring in nature as it could form by a

number of natural causes involving wildfire, thunder strikes, volcanic activities, and meteorite impact. In view of the novelty of shungite mineral, however, the major process of transformation of soot into shungite must be novel as well. Indeed, in order to effect direct conversion of **3** into **1** (dotted arrow), it is necessary to heat **3** to higher than 2,500°C. This range of temperature occur not very often in nature, and even if occurred only for very short-periods of time as in the cases of meteorite crush or volcano eruption. Stepwise process (**3**→**4**→**2**→**1**) also demands extremely high energy sources, and not very likely to occur in nature. In conclusion the soot theory on the origin of shungite seems likely at first but the intermediate processes are hard to imagine.

The other noteworthy points shared by both shungite and soot concerns the occurrence of C₆₀ in these carbons. According to our interpretations on the structure and growth mechanism of the primary particle of soot [2], every primary particle contains one C₆₀ molecule in its core. Hence at least in the beginning, considerably high amounts of C₆₀ could have been there before soot is converted into shungite. The reason for the presence of *ca* 20 ppm of C₆₀ in shungite [4] is still unknown, but the chance of some of C₆₀ contents getting out of the shells of primary particles has already been mentioned above.

Finally it should be noted that the level of abundance of C₆₀ found in shungite[4] definitely exceeds the controversial level of less than 1 ppm, often invoked doubts on the results in the past[5-7].

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Hydrothermal Treatment of Shungite Rock

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<Introduction>

Shungite produced in Karelia of north-west Russia is a natural rock including carbon and is classified by the carbon content into following five groups; Type I (75-98 mass%C), Type II (35-75 mass%C), Type III (20-35 mass%C), Type IV (10-20 mass%C), Type V (below 10 mass%C). A few researchers studied on the carbon in Shungite. A.K. Boldyrev, G.A. Kovalev reported that carbon in Shungite was poor crystalline graphite, and K. Usenbayev et al. concluded that Shungite had graphene layers but was non-graphitizing carbon because graphitization did not occur by heat treatment of Shungite.⁽¹⁾ Recently, the micro structure of carbon in Shungite has been explicated by the electron microscopy.⁽²⁾ As a summery, it has been pointed out that the carbon in Shungite has a turbostratic structure with graphene layers and includes a small amount of single- or multi-layered spherical super fine particles such as fullerene.

Shungite especially with low content of carbon usually includes a large amount of low quartz, which suggests that hydrothermal fluid had some effect on Shungite formation. In this study, the carbon of Shungite was hydrothermally treated at high temperatures to estimate the effect of hydrothermal fluid on the formation of Shungite.

<Experimental>

Shungite Rock Type I collected from Maksova, Karelia, Russia, was used as a starting material. X-ray fluorescence analysis (XRF) showed that Shungite contained SiO₂ and various metal oxides. In order to purify the carbon in Shungite, Shungite rock (3.0 g) was crashed to powder and hydrothermally treated in 20% HF and 1.0M NaOH (17.5 ml) at 180°C for 24hours. The hydrothermal treatments were repeated in several times. The products were washed with water and dried at 100°C. High temperature hydrothermal treatments of the carbon in Shungite were carried out up to 800°C at 100 MPa for 24 hours in pure water (80 ml). The purified Shungite carbon (20mg) was sealed in Pt capsules (2.8 mm in inner diameter, 40 mm in height) together with water and heated in test tube type autoclaves. Temperature was measured on the wall of the autoclaves. Powders of carbon black and graphite were also hydrothermally treated as a reference. The product was characterized by XRD, Raman spectroscopy, SEM, EDX and TEM.

<Results>

Figure 1 shows the XRD patterns of Shungite hydrothermally treated at 180°C. The XRD pattern of the original Shungite included strong diffractions of low-quartz. These peaks were disappeared and two broad peaks with low intensity which can be assigned to graphite appeared on around 26 and 44 degree after hydrothermal treatments. The intensities of these two peaks increased as the number of times of the hydrothermal treatment increased, which was caused by removal of SiO₂ and other impurities. Analysis of XRF and microscopic EDX showed that the final sample (d) included only carbon without any other impurities.

The hydrothermal treatments of the purified Shungite carbon at high temperatures did not give any changes in XRD patterns (Fig. 2), which suggests that the hydrothermal treatment even at 800°C had no effect on long order of carbon structure of Shungite. Two distorted peaks were observed in Raman spectra, and the intensity ratio of these peaks changed by high temperature treatments over 600°C. It is considered that Shungite was formed at low temperatures below 600°C under hydrothermal conditions. The change at high temperatures above 600°C might be explained by oxidation of amorphous carbon under hydrothermal conditions.

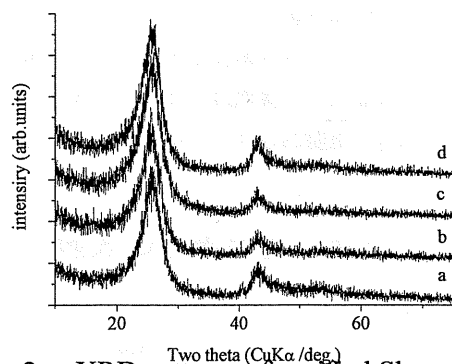


Fig. 2. XRD patterns of purified Shungite (a) and samples hydrothermally treated at (b) 500°C, (c) 600°C, and (d) 700°C.

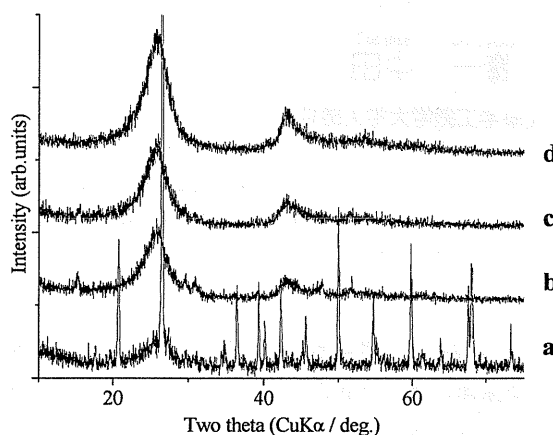


Fig. 1. XRD patterns of Shungite (a) and samples obtained by hydrothermal treatment. (b): treatment of the original Shungite in NaOH and HF soln., (c): treatment of sample (b) in HF soln., (d): treatment of sample (c) in NaOH and HF soln.

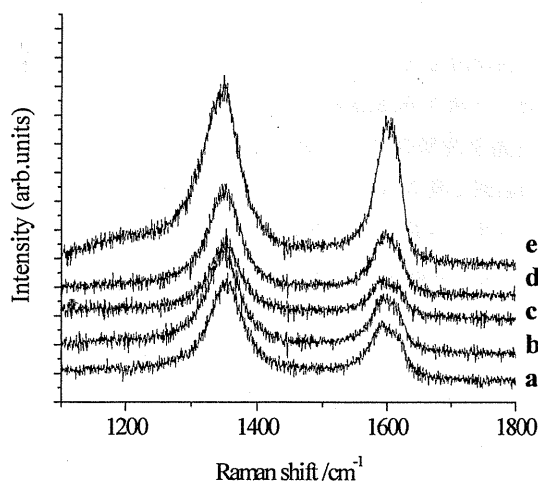


Fig. 3. Raman spectra of purified Shungite (a) and samples hydrothermally treated at (b) 500°C, (c) 600°C, (d) 700°C, and (e) 800°C.

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